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REACTIONS OF PORPHYRINS IN SURFACTANT ASSEMBLIES
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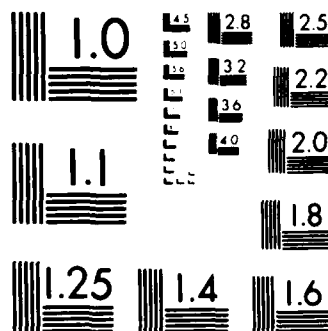
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REACTIONS OF PORPHYRINS IN SURFACTANT ASSEMBLIES, MICROEMULSIONS
AND IN SOLUTIONS

FINAL REPORT

DAVID G. WHITTEN

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17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Our ARO-sponsored research has focused on three different areas, all of which center around photochemical reactions occurring in microheterogeneous media. The first area of investigation has been of photoisomerizations and related processes occurring in spread monolayer films at the air-water interface as well as in supported multilayer assemblies. Our studies in this area have demonstrated that reactivity in the spread films can be profoundly different from that occurring in solution. Moreover we have been able to investigate systematically specific factors such as the effect of film compression and the presence of various liquids such as water within or in contact with the film or assembly. A number of our findings in this area have been published and more publications will result from studies not yet completed. We have also studied extensively reactions occurring across an interface. Specifically we have examined photooxidations which are initiated from a light-absorbing sensitizer contained in a film or an assembly but have the chemical consequence of reaction of a (cont'd)			
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solute either contained at a different site in the assembly or present in a contacting aqueous or mixed aqueous-organic solution. While we have found that these interface-spanning reactions can be quite efficient in certain cases, we have also investigated extensively environmental factors which can retard or eliminate them. Most of the reactions that we have investigated thus far originated by sensitization of singlet oxygen, a highly reactive but relatively short-lived reagent. Singlet oxygen has been found to migrate with relative ease through a number of different media, although we find that penetration of highly condensed or compressed films clearly retards the migration of the active oxygen, at least during its excited state lifetime. Although we have used a variety of light-absorbing molecules to initiate these reactions, most of our studies have focused on some synthetic porphyrins which absorb relatively strongly in the visible and near ultraviolet regions. These porphyrins have been specifically designed and synthesized due to their excellent film-forming abilities.

The synthetic porphyrins that we have used exist as various stereoisomers; the third part of our studies has been an investigation of the reactivities of these various stereoisomers of synthetic porphyrins at interfaces. We have been particularly interested in the relative ability of these porphyrins to be incorporated in or pass through an interface such as that formed when phospholipids are dispersed in water. We have found that the reactivity of different porphyrin stereoisomers at interfaces differs dramatically from that observed in solution. For example, we find the porphyrins are much stronger bases at anionic interfaces and undergo metal ion incorporation, in some cases, several orders of magnitude more rapidly than in solution. Preliminary results suggest that the different behavior of porphyrin stereoisomers can be largely associated to different differential orientation at charged interfaces. This should result in pronounced differences in the ability of the porphyrins to act as photosensitizers in a number of different photochemical reactions.

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